



# Trichloroethylene adsorption by activated carbon preloaded with humic substances: effects of solution chemistry

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## Abstract

Trichloroethylene (TCE) adsorption by activated carbon previously loaded (“preloaded”) with humic substances was found to decrease with increasing concentrations of monovalent ions (NaCl), calcium (until solubility was exceeded), or dissolved oxygen in the preloading solution. For a given percentage of organic carbon removal during humic acid loading, greater reductions in TCE adsorption occurred with increasing monovalent ion concentration and calcium concentration at constant ionic strength. However, this effect was related primarily to the amount of humic material adsorbed—the reduction in TCE adsorption was independent of the ionic composition of the preloading solution when compared at similar humic acid loading. Experiments were performed which showed that calcium ions can associate with humic material after the humic has been adsorbed, which subsequently reduces TCE uptake, but this effect does not dominate when calcium is present during humic loading. At sufficiently high calcium concentrations (approaching solubility), aggregation or co-precipitation of humic acid mitigated the effects of preloading. In contrast to the effects of ionic composition, the presence of dissolved oxygen *did* fundamentally change the mechanism by which organic macromolecules compete with TCE. TCE uptake was lower when preloading by poly(maleic acid) (PMA) occurred in the presence of dissolved oxygen, even when the amount loaded was the same. One explanation invokes a coupling mechanism promoted by the carbon surface, which results in either additional blockage of TCE sorption sites, additional site competition, or both. In all experiments, the effects of preloading were consistent with those reported previously, which have been interpreted as a loss of high-energy sites available to TCE, causing a significant reduction in the site-energy heterogeneity, and reduced uptake in the low concentration region. © 2002 Elsevier Science Ltd. All rights reserved.

**Keywords:** Trichloroethylene; Preloading; Adsorption; Activated carbon; Humic acid; Water chemistry

## 1. Introduction

Activated carbon, in both granular (GAC) and powdered (PAC) forms, is widely employed to remove synthetic organic contaminants (SOCs) from potable water supplies, because it has the ability to remove a broad range of organic compounds effectively, and

because it can protect water supplies from transient loading of toxic compounds (e.g. [1]). A factor complicating the design and implementation of activated carbon for the treatment of potable waters is the presence of naturally occurring dissolved and colloidal organic matter (NOM). The presence of NOM can significantly reduce the efficiency of activated carbon processes, by competing with targeted SOCs for adsorption sites, and thus reducing SOC uptake and rate of adsorption. The simultaneous competitive adsorption of NOM and a range of different SOCs has been observed in many studies employing batch

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isotherm experiments, in which activated carbon is contacted with a solution containing both the target SOC and NOM [2–17]. In many of these studies, model compounds, typically humic and fulvic acids, have been used to simulate the effects of NOM from natural waters, because these components of NOM are thought to be responsible for much of its reactivity.

In fixed-bed reactors, the mass-transfer zone of NOM components can move more rapidly than that of the targeted SOC. Therefore, at some positions within the bed, the NOM adsorbs from an SOC-free solution, and fouls or “preloads” the carbon ahead of the pollutant. It has been shown that the preloading phenomenon can significantly reduce the performance of fixed bed adsorbers [10,14–17,18–22]. This results from a reduction in equilibrium uptake of SOC, caused by direct competition for adsorption sites, pore blockage or both [6,7,23]. In addition, a reduction in the rate of SOC adsorption is often observed, which may include an increased diffusion resistance at the particle surface [10], an intraparticle diffusion resistance (e.g., [17,18]), or both. Because preloaded NOM can slowly change the adsorptive properties of GAC over time, predictive design is made more difficult.

Several factors could potentially influence the impact of preloading on adsorber performance. One such factor is the composition of the background NOM; for example, in many systems the effect of preloaded organic matter on SOC uptake is related to the amount of the smaller size fraction adsorbed [8,24]. Characteristics of the adsorbent, especially the pore size distribution [25] and surface functional group composition, may also be important. Solution chemistry (including ionic composition and dissolved oxygen) has been shown to play an important role in the adsorption of humic and fulvic acids by activated carbon, and would be expected to influence preloading phenomena. However, no study in the literature has addressed the effect of solution chemistry on the impacts of preloading. This research was conducted to investigate the effects of ionic strength, calcium ion concentration, and dissolved oxygen on the adsorption of trichloroethylene (TCE) by activated carbon preloaded with humic substances. TCE was chosen because it is a widespread contaminant, it has been designated as a priority pollutant by the US EPA, it is regulated by the Safe Drinking Water Act, and it can be accurately quantified using gas chromatography with electron capture detection.

It has been shown previously that increasing monovalent ion concentration (expressed as ionic strength) increases the extent of humic acid adsorption [26–31]. The effects of monovalent ions include screening charge on humic acid functional groups (e.g., carboxylic), which can cause a reduction in the initial size distribution of the humic substances. This phenomenon can be measured directly using ultrafiltration and indirectly size

exclusion chromatography [32,33,54]. In addition, monovalent ions can screen charge on the adsorbent surface, tending to reduce specific interactions, whether attractive or repulsive. Whether this mechanism will tend to increase or decrease uptake of humic acid will depend on the adsorbent surface charge and the humic acid functionality.

As a result of increased humic acid sorption in response to increased solution ionic strength, a smaller adsorbent dose is required to remove a desired percentage of the initial TOC, resulting in an increased amount of organic carbon adsorbed. Therefore, it is hypothesized that for a given percentage of organic carbon removal from solution, greater reductions in TCE adsorption would occur with increasing ionic strength. From a more mechanistic point of view, it is also necessary to identify whether the effects of preloading are similar under different ionic strengths, but at comparable organic matter loading. For a given amount of humic acid loading, the equilibrium concentration of organic carbon will be lower when the ionic strength is high, and a greater fraction of the initial organic carbon will have been adsorbed. As a result, the molecular weight distribution of components remaining in solution, and consequently the distribution of those adsorbed, will be shifted [32]. This research was designed to determine whether this shift in molecular weight, at constant loading, influences the impact of humic acid preloading on TCE uptake.

Calcium is the principal cation in most surface and groundwater [34]. Interactions between calcium and humic substances have been studied extensively by soil scientists (e.g., [35,36]) and geochemists (e.g., [55]). The ability of calcium ion to increase the extent of humic substance adsorption by oxides (e.g. [37]) and activated carbons [29,31,38–40] has been demonstrated in prior research. The effects of calcium ions include screening charge on humic acid functional groups, neutralizing charge on the adsorbent surface, and possibly creating new adsorption sites via cation bridges between negatively charged surface functional groups and humic acid moieties. If the dominant effect of calcium is to reduce the size of humic molecules through charge screening and to create new adsorption sites for humic acid through cation bridges on the adsorbent surface, it is conceivable that the impacts of preloading on TCE uptake may be exacerbated. However, calcium ions can cause aggregation in solution (e.g., [33,41,55]) through cationic bridging between humic molecules in solution, the formation of calcium-humic complexes, or both. At sufficiently high concentrations, precipitation may occur. If the dominant effect of calcium were to cause aggregation of small humic acid components in solution, the ability of humic acid access to micro- and mesopores would be reduced, which could conceivably reduce the impacts of preloading. Therefore, an objective of this

research was to compare the effects of mono- and divalent cations on the impacts of preloading.

Studies of NOM sorption from lake [42] and river [43] water, and of model and natural humic and fulvic acids from aqueous solution [44–46], have shown varying sensitivity to the concentration of dissolved oxygen. The presence of oxygen tends to enhance the uptake of natural organic matter, in a manner that is analogous to the effects of oxygen on the sorption of phenolic compounds. Such compounds are thought to undergo oxidative coupling reactions that are catalyzed by carbon surfaces, which increase their uptake [42,46–48]. Karanfil et al. [45] showed that the effects of dissolved oxygen on the uptake of dissolved organic matter correlated with the content of acidic groups having  $pK_a$  values above 8.0. It is likely that these groups include some phenolic moieties. If the effects of dissolved oxygen on the uptake of NOM are related to their coupling in the sorbed phase, it is possible that the presence of dissolved oxygen may have an impact on subsequent competitive interactions with the targeted SOC. In addition, consumption of oxygen as a result of uptake by activated carbon itself, as well as by microbial activity, may create an oxygen gradient within a fixed-bed adsorber. Therefore, the uptake of TCE by carbon preloaded in the presence and absence of dissolved oxygen is compared.

## 2. Methods and materials

### 2.1. Sorbates

Humic acid extracted from a Laurentian soil, and poly(maleic acid) (PMA), synthesized in a previous study [4], were used as model reactive components of NOM. PMA was chosen to investigate the impacts of preloading under oxic and anoxic conditions because its uptake had been previously identified as sensitive to the presence of dissolved oxygen [46]. Humic acid was received as a dry powder (Fredriks, The Netherlands). Stock solutions for preloading experiments were prepared by dissolving humic materials and PMA in distilled and de-ionized water at elevated pH. After dissolution, the pH was adjusted to  $7.0 \pm 0.1$  with HCl, and the solution was filtered through a  $0.45 \mu\text{m}$  polysulfone filter prior to refrigerated storage. Stock solutions of reagent grade (pesticide free) TCE were prepared in methanol. Working solutions were prepared by spiking background water with stock solution to achieve the desired initial concentration of solute.

The molecular weights of the Laurentian humic acid and PMA were determined using High Pressure Size Exclusion Chromatography calibrated with poly(styrene) sulfonate [32]. The weight- and number-averaged molecular weights of the humic acid were 5465 and 1861,

respectively. The modal molecular weight (chromatogram peak) was 2580. The weight- and number-averaged molecular weights of the PMA were 2612 and 2006, respectively.

### 2.2. Activated carbon

The activated carbon used in this research (F400, Calgon, Pittsburgh, PA) is a microporous adsorbent, with about 91% of the surface area in pores having widths less than 2 nm, and with only about 15% of the surface area in pores having widths greater than 20 nm. This adsorbent has a  $\text{pH}_{\text{pzc}}$  of about 9.5, and therefore had a net positive charge at the pH values used in this research. For additional details concerning the characterization of this carbon, see Karanfil and Kilduff [49]. Carbon received from the manufacturer was crushed and mechanically sieved to a uniform particle size (mean diameter of  $165 \mu\text{m}$ ) using US standard sieves. Carbon was washed, sonicated to remove fines, oven dried at  $105^\circ\text{C}$  to constant weight, and stored in a desiccator until use.

### 2.3. Humic substance preloading

Preloading with Laurentian humic acid was done in 1 L amber-colored glass bottles. Preloading reactors had sufficient headspace to assure that the sorption took place under oxic conditions; i.e., dissolved oxygen was not limiting. Preloading with PMA was done in 160 mL bottles. To assure oxic conditions, 60 mL of headspace was provided, and measurements at the completion of the preloading experiment confirmed that dissolved oxygen was present in excess. To assure anoxic conditions, bottles were completely filled with a nitrogen-purged stock solution in an anaerobic chamber. For all experiments, the humic acid concentrations ranged from 15 to 60 mg DOC/L, and GAC doses ranged were generally 1.05 g/L. The pH of all preloading reactors was kept constant at pH 7 with  $10^{-3}\text{M}$  phosphate buffer. Sodium azide (0.0015 M) was used to control biological activity. Calcium ion concentration was controlled by adding the chloride salt. Ionic strength was adjusted to the desired concentration (either 0.01, 0.05 or 0.10 M) using NaCl. For all experiments, carbon was equilibrated for 30 days.

At environmental temperatures and pressures, the theoretical solubility of calcium (aragonite,  $\text{CaCO}_3$ ) in a system open to the atmosphere is about 0.50 mM (20 mg/L as  $\text{Ca}^{2+}$ ). However, in the presence of humic acid, an initial calcium concentration of 0.50 mM or less was expected to result in free calcium concentrations well below solubility [33]. The experiments were conducted in the absence of phosphate buffer to avoid confounding effects from the potential precipitation of hydroxyapatite. Two experiments were conducted with

initial calcium concentrations greater than 0.50 mM (20 mg/L) in an attempt to exceed calcium solubility to investigate the potential impacts of precipitate formation. A brown precipitate was observed in both reactors.

For all preloading experiments, carbon was recovered after equilibration by vacuum filtration on a 0.2 µm filter, dried under vacuum in a desiccator at room temperature for a period of 14 days, a time sufficient to reduce the moisture content to below measurable levels, and stored in a desiccator under vacuum until use. Speth [21] found that neither washing, mechanically scouring, nor drying by vacuum desiccation, in any way mitigated the impacts of preloading. Humic acid concentrations were quantified by total organic carbon (TOC) analysis (TOC 500 Shimadzu Corporation, Japan) and UV spectrophotometry (Varian Optical, Victoria, Australia).

#### 2.4. Adsorption isotherms

Uptake of TCE by as-received and preloaded GAC was measured in completely mixed batch reactors [50]. First, carbon (10–15 mg) was added to buffer solution in 250 mL amber-colored glass bottles. The reactors were then spiked with a TCE stock solution to yield initial concentrations ranging from 0.030 to 8 mg/L. Finally, reactors were carefully filled to completely eliminate headspace and sealed with Teflon-lined septa. For the oxic isotherms, pure oxygen was used to supersaturate buffer solution with oxygen (DO ~ 30 mg/L) and no headspace was left in the bottles. For the anoxic conditions, nitrogen purged (oxygen-free) solutions were used and the isotherm bottles were filled and spiked with TCE in an anaerobic chamber.

Isotherm conditions were designed to result in equilibrium solution phase concentrations starting from below the drinking water limit of 5 µg/L, and spanning several orders of magnitude. While not directly evaluated in this work, Carter et al. [4] have confirmed that the measured isotherm does not depend on the initial TCE concentration under these conditions. Because the preloaded carbon was not exposed to fresh humic acid solution, all competition was from pre-adsorbed organic matter. Preliminary desorption studies confirmed that preloaded humic acid did not desorb under these conditions to any measurable extent, a finding consistent with others [30]. Preliminary rate studies indicated that two weeks was sufficient time to reach equilibrium based on measurements of TCE solution phase concentrations. This equilibrium state should be considered operational because it is possible that TCE transport may proceed for extended periods of time without causing measurable changes in solution phase concentrations.

After equilibration, samples were extracted into hexane for quantification by a gas chromatography using electron-capture detection. Precision for TCE

analysis including the extraction step was 3% or better. Losses resulting from volatilization, sorption onto reactor components, or bacterial activity were less than 5% in control reactors which did not contain adsorbent; no attempt was made to correct for them.

#### 2.5. Modeling single-solute adsorption equilibria

The two-parameter Freundlich equation has enjoyed widespread use in water treatment applications. While this model could not capture the curvature exhibited by the data (on log–log coordinates), which spanned several orders of magnitude in concentration, it was possible to accurately fit data having  $C_e$  below about 100 µg/L. The Freundlich equation is written:

$$q_e = K_F C_e^n, \quad (1)$$

where  $q_e$  is the amount adsorbed at equilibrium (normalized to adsorbent mass),  $C_e$  is the equilibrium solution phase concentration,  $K_F$  is considered a capacity parameter, in the sense that it reflects the uptake corresponding to a value of  $C_e$  equal to unity (in whatever concentration units chosen), and  $n$  is a dimensionless parameter related to the site energy distribution. An advantage of the Freundlich equation compared to three-parameter isotherm models is that its two parameters can be estimated with greater statistical significance (narrower confidence limits). Therefore, changes in isotherm parameters that result from preloading are more clearly identified and are more robust. Advantages of three-parameter isotherms include a better fit to data over wide ranges in concentration, facilitating visual comparison, and accurate estimation of the uptake at any specified value of  $C_e$ . The three-parameter Dubinin–Astakhov model was chosen because it exhibited low residual sum-of-squares (SSR) when log-transformed experimental data were fitted using a non-linear least-squares regression analysis. This isotherm is written as

$$q_e = Q^0 \exp \left[ \frac{-(RT \ln(C_{\text{sat}}/C_e))^n}{B} \right], \quad (2)$$

where  $C_{\text{sat}}$  is the TCE solubility (1100 mg/L);  $Q^0$ ,  $B$  and  $n$  are empirically determined parameters; and other terms are as previously defined. The efficacy of the Dubinin model in fitting representative adsorption data is demonstrated in Fig. 1.

### 3. Results and discussion

#### 3.1. Impacts of preloading

The impact of preloading on TCE uptake is shown by the isotherms plotted in Fig. 1; experimental conditions and isotherm model parameters determined from non-

linear regression of experimental data are shown in Table 1. TCE uptake by carbon preloaded with humic acid is significantly lower than uptake by as-received carbon. The relative reduction in uptake is greater in the

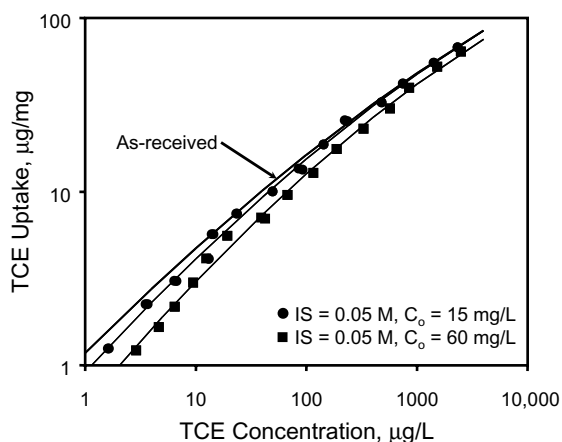


Fig. 1. TCE uptake by preloaded F400 carbon, showing the effect of preloading. Lines represent fits to adsorption data using the Dubinin–Astakhov isotherm.

low concentration region of the isotherm; as a result, the Freundlich  $K_F$  decreases and  $n$  increases with preloading. The decrease in the Freundlich  $K_F$  is statistically significant for both isotherms shown (i.e., confidence intervals do not overlap), and the increase in  $n$  is statistically significant for the carbon preloaded using the higher humic acid solution concentration. The observed trends are consistent with those reported previously, which have been interpreted as a loss of high energy sites available to TCE, causing a significant reduction in the site-energy heterogeneity, and reduced uptake in the low concentration region [4,6–8]. At higher levels of preloading, further changes in the site-energy heterogeneity are distributed across a wide spectrum of site energies, suggesting a lowering of the average site energy, a reduction in the total number of sites, or both.

The effect of the initial humic acid solution concentration (at constant ionic strength) on the impact of preloading is also shown in Fig. 1. When the initial concentration is increased at a constant adsorbent dose, the loading of humic acid increases (Table 1), and the molecular weight distribution of adsorbed humic acid shifts to smaller values. This shift occurs because as the initial concentration of humic acid is increased relative

Table 1  
Effect of ionic strength on HA preloading

Preloading conditions			Dubinin isotherm parameters and statistics			Freundlich isotherm parameters and statistics		
IS, M <sup>a</sup>	C <sub>0</sub> , mg TOC/L	q <sub>e</sub> , mg TOC/g	Param.	Param. Est. <sup>b</sup>	95% CI <sup>c</sup>	Param.	Param. Est. <sup>b</sup>	95% CI <sup>c</sup>
0.01	0.0	0.0	$Q^0$	342	231–453	$K_F$	1.26	1.19–1.34
			$n$	1.55	1.38–1.71	$n$	0.566	0.545–0.586
			$B$	42.1	15.6–68.6			
0.05	15.2	12.7	$Q^0$	314	177–451	$K_F$	1.01	0.893–1.14
			$n$	1.64	1.42–1.87	$n$	0.596	0.553–0.640
			$B$	57.8	7.47–108			
0.05	30.6	20.5	$Q^0$	500	153–847	$K_F$	0.862	0.764–0.973
			$n$	1.40	1.14–1.66	$n$	0.604	0.562–0.646
			$B$	22.2	0.0–44.9			
0.05	60.9	25.4	$Q^0$	273	143–403	$K_F$	0.650	0.548–0.771
			$n$	1.73	1.46–1.99	$n$	0.666	0.603–0.729
			$B$	73.4	0.0–147			
0.10	15.3	13.3	$Q^0$	351	84–617	$K_F$	0.868	0.742–1.02
			$n$	1.54	1.19–1.89	$n$	0.596	0.541–0.650
			$B$	38.6	0.0–90.5			
0.10	30.7	21.9	$Q^0$	209	90.0–329	$K_F$	0.733	0.600–0.895
			$n$	1.91	1.52–2.31	$n$	0.653	0.583–0.723
			$B$	150	0.0–371			
0.10	62.2	29.9	$Q^0$	243	143–342	$K_F$	0.587	0.518–0.665
			$n$	1.83	1.58–2.08	$n$	0.663	0.619–0.707
			$B$	105	6.14–203			

<sup>a</sup> IS: Ionic strength.

<sup>b</sup> Isotherm parameters correspond to uptake in units of µg/mg and concentration in units of µg/L.

<sup>c</sup> CI: Confidence interval.

Conditions: Calcium content was zero in all preloading and isotherm reactors.

Adsorbent dose was 1.05 g/L for all preloading reactors.

to the adsorbent dose (increasing  $C_0/D_0$ ), a greater amount of the most adsorbable components are initially present in solution, and are subsequently adsorbed. For the relatively hydrophobic humic substances studied here, the most adsorbable components were shown to be the lowest molecular weight compounds [32].

### 3.2. Effects of monovalent ion concentration during preloading

The impact of monovalent ion concentration on TCE uptake by preloaded carbon is shown in Fig. 2. Lines are fits to the adsorption data using the Dubinin–Astakhov isotherm; data were not shown to increase the clarity of the figure. Experimental conditions and isotherm model parameters are shown in Table 1. In this Figure, isotherm model fits are shown for TCE uptake by carbon loaded using the same initial humic acid solution concentration ( $\sim 60$  mg/L) and adsorbent dose ( $D_0 = 1.05$  g/L), but different monovalent ion concentrations, expressed in terms of ionic strength. A consistent decrease in TCE uptake is observed with increasing ionic strength. Relative to the as-received isotherm, the reduction in  $K_F$  was statistically significant for all the isotherms on preloaded carbon shown in Fig. 2; however, the increase in  $n$  was significant only when the carbon was preloaded at the two higher ionic strengths. A significant increase in humic acid loading, and concomitant increase in the loss of high-energy sites available for TCE adsorption, occurred as a result of increasing ionic strength alone. This can be explained by a decrease in the molecular size distribution of humic acid components initially present in solution [33]. As a result of this shift in the size distribution, there is an

increase in the concentration of humic components small enough to access adsorbent micro- and mesopores, in turn increasing the uptake of humic acid from solution. Support for such an explanation follows from a comparison of carbon pore dimensions with the size of humic molecules.

A large fraction of the total surface area of the F400 activated carbon is contained in micropores having widths less than about 2 nm. Evidence from the literature suggests that humic molecule sizes are of the same order of magnitude. For example, Cameron et al. [51] using ultracentrifugation, found that humic substance radii of gyration of 1.5, 2.0 and 3.2 nm corresponded to molecular weights of 2600, 4400, and 12,800 respectively. Using small-angle X-ray scattering, Thurman et al. [52] estimated the radii of gyration of humic substances to be on the order of 0.5–3.3 nm, corresponding to a molecular weight range of 500 to greater than 10,000 g/mol. Aiken and Malcolm [53] found radii of gyration for aquatic fulvic substances ranging from 0.45 to 0.88 nm, corresponding to molecular weights ranging from about 500–1000 g/mol. These results suggest that humic acid components having molecular weights greater than about 1500 kDa are larger than 2 nm and cannot access adsorbent micropores to compete with TCE adsorption. In previous work, we studied the molecular weights of Laurentian humic acid fractionated by ultrafiltration. The smallest fraction, those passing a 3 kDa molecular weight cutoff ultrafiltration membrane, had a weight-averaged molecular weight of 1400 Da as PSS, determined by size exclusion chromatography. These components comprised about 20% of the humic acid by mass. The next largest fraction, which passed a 10 kDa membrane, but was retained on the 3 kDa membrane, had a molecular weight of about 2700 Da. It appears likely, therefore, that under low ionic strength conditions, larger humic fractions could not access a significant percentage of the carbon surface area, and consequently could not compete directly with TCE for adsorption sites. (Physical blockage of pore throats did not appear to be a significant mechanism of competition for the larger humic materials). Increasing the ionic strength, and decreasing the size distribution of humic acid, significantly increased the concentration of humic components small enough to access adsorbent micropores and compete with TCE for adsorption sites.

The effects of preloading illustrated by the isotherms shown in Figs. 1 and 2 were associated with a change in the loading of humic acid. An important question to resolve is whether increases in ionic strength fundamentally change the way in which adsorbed humic acid competes with TCE. Previous research has shown that when carbons are preloaded with higher concentrations of Laurentian humic acid (increasing  $C_0/D_0$ ), the adsorbed molecular weight distribution shifts to smaller

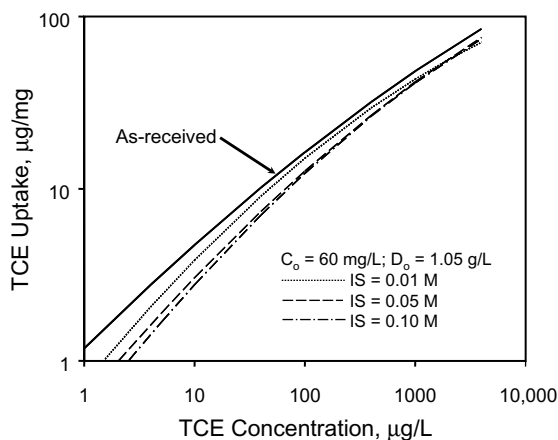


Fig. 2. The impact of ionic strength on TCE uptake by F400 carbon preloaded with Laurentian humic acid. Lines are fits to adsorption data using the Dubinin–Astakhov isotherm; data is not shown to increase the clarity of the figure.

values [32]. Under such conditions, reductions in TCE uptake correlated (primarily) with humic acid loading [8]. However, increasing the ionic strength during preloading causes a reduction in the molecular *size* (and size distribution) of humic substances, making them more adsorbable. As a result, for the same amount of humic acid preloaded, the equilibrium concentration of organic carbon will be lower when the ionic strength is high; therefore, and a greater fraction of the initial organic carbon will have been adsorbed. Therefore, the molecular *weight* distribution of components remaining in solution, and consequently the distribution of those adsorbed, will be shifted to *higher* values [33]. The higher molecular weight species, now made smaller and more adsorbable by virtue of conformation changes resulting from increases in ionic strength, could possibly exhibit a greater impact on TCE uptake.

Fig. 3 shows TCE uptake by carbon preloaded at different ionic strengths, and different initial humic acid solution concentrations, but yielding similar humic acid loading. These data suggest that ionic strength does not fundamentally change the mechanism by which humic acid competes with TCE; rather, the impact on TCE uptake is similar when the humic acid loading is the same. Similar results were found at lower humic acid loadings (data not shown). This was evaluated further by plotting TCE uptake by preloaded carbon as a fraction of the as-received uptake at the same  $C_e$ , versus the uptake of humic acid as organic carbon (Fig. 4). This allowed a comparison among a large number of isotherms, including those corresponding to preloading at  $IS=0.01$  reported previously [8]. TCE uptake

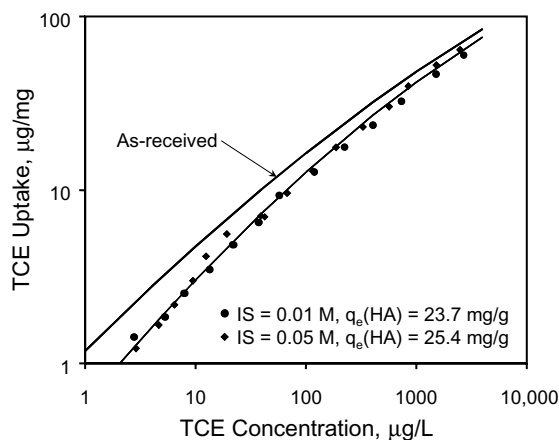


Fig. 3. TCE uptake by carbon preloaded at different ionic strengths, and different initial humic acid solution concentrations, but yielding similar humic acid loadings. Lines represent the Dubinin–Astakhov isotherm fitted to pooled data. The isotherms measured at ionic strength ( $IS$ ) = 0.05 M are compared to those measured at  $IS=0.01$  M reported by Kilduff et al. [8].

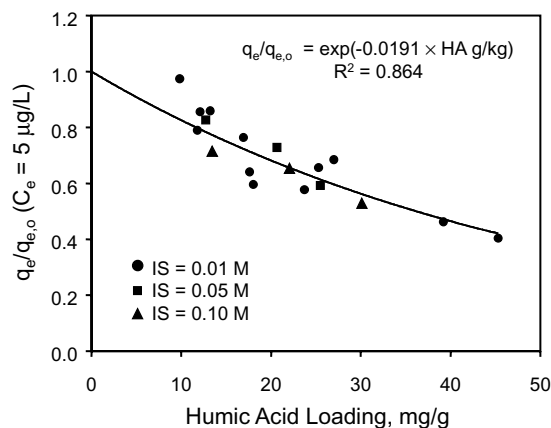


Fig. 4. The effect of preloading is evaluated in terms of TCE uptake by preloaded carbon, as a fraction of the as-received uptake,  $q_e/q_{e,0}$ , both evaluated at the US drinking water standard of  $C_e = 5 \text{ mg/m}^3$ . The reduction in TCE uptake by carbons preloaded at ionic strengths ( $IS$ ) of 0.01 M (●), 0.05 M (■), and 0.10 M (▲). Line shown is an empirical correlation to describe the parametric trend. Data for  $IS=0.01$  M are those reported by Kilduff et al. [8]. Solution composition for all data shown:  $1 \times 10^{-3}$  M phosphate buffer, 0.0015 M sodium azide, pH 7.

corresponding to a solution phase equilibrium concentration of  $5 \mu\text{g/L}$ , the US drinking water standard, was chosen as a basis for comparison. As shown in Fig. 4, the reduction in TCE uptake by carbons preloaded at ionic strengths ranging from 0.01 to 0.10 M is well-correlated with the amount of humic material adsorbed, and does not depend on the ionic strength conditions during preloading. Therefore, when the amount of adsorbed humic acid was similar, isotherm parameters (e.g., Freundlich  $K_F$  and  $n$  values) were statistically similar for all ionic strength conditions. These results suggest that the increases in ionic strength, which cause (1) decreases in the initial molecular-*size* distribution of humic acid in solution, (2) increases in the adsorbed molecular *weight* distribution, and (3) increases in the extent of humic adsorption, do not appear to change the way in which humic acids compete with TCE.

Some water treatment systems may target removal of NOM (with treatment goals generally specified as a percentage of source water TOC removal) in addition to SOC (which generally have treatment goals specified in terms of compound-specific drinking water standards). Therefore, it is of interest to evaluate the effects of ionic strength on the impacts of preloading for the same removal of organic carbon from the solution phase. In Fig. 5, the data presented in Fig. 4 (fraction of uptake by as-received carbon at the same  $C_e$ ) were plotted versus the removal of organic carbon (i.e., TOC) from solution ( $1 - C_e/C_0$ ). Clearly different trends are observed for each ionic strength, ranging from 0.01 to 0.10 M. For a

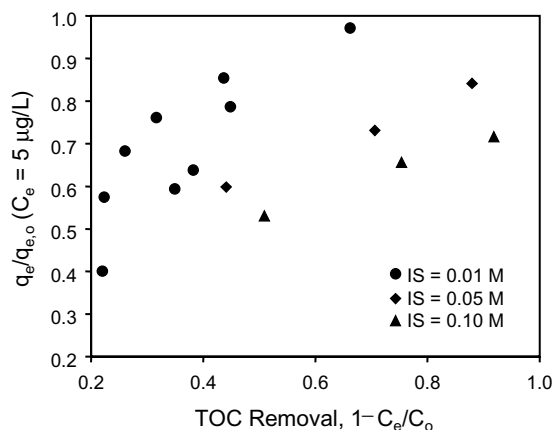


Fig. 5. The effect of preloading is evaluated in terms of TCE uptake by preloaded carbon, as a fraction of the as-received uptake,  $q_e/q_{e,0}$ , both evaluated at the US drinking water standard of  $C_e = 5 \text{ mg/m}^3$ . For the same organic carbon removal from solution, uptake by preloaded carbon decreases with increasing ionic strength of the preloading solution. Solution composition for all data shown:  $1 \times 10^{-3} \text{ M}$  phosphate buffer,  $0.0015 \text{ M}$  sodium azide, pH 7.

given TOC removal, NOM loading is greater under higher ionic strength conditions, causing greater reductions in TCE adsorption.

If the  $q_e/q_{e,0}$  trends observed for the high ionic strength conditions as plotted in Fig. 5 are extrapolated to lower humic acid removals, the data for all ionic strengths appear to converge. Low humic acid removals correspond to high  $C_e/D_0$  ratios, when only the smallest molecular-size components are adsorbed [32]. Therefore, increases in ionic strength have a smaller effect when the supply of smaller, more adsorbable components in solution is large compared to the adsorbent capacity.

### 3.3. Effects of divalent ion concentration during preloading

In this work, we have focused our investigation on the impacts of a single divalent ion, calcium. Fig. 6 shows isotherms measured using carbon preloaded at different ionic strengths, calcium concentrations, and initial humic acid solution concentrations, but yielding similar humic acid loading. Experimental conditions and isotherm model parameters determined from non-linear regression of experimental data are shown in Table 2. As with the effects of changes in ionic strength resulting from the concentration of monovalent ions (NaCl), these data suggest that the presence of a divalent cation does not fundamentally change the mechanism by which humic acid competes with TCE; rather, the impact on TCE uptake is similar when the humic acid loading is

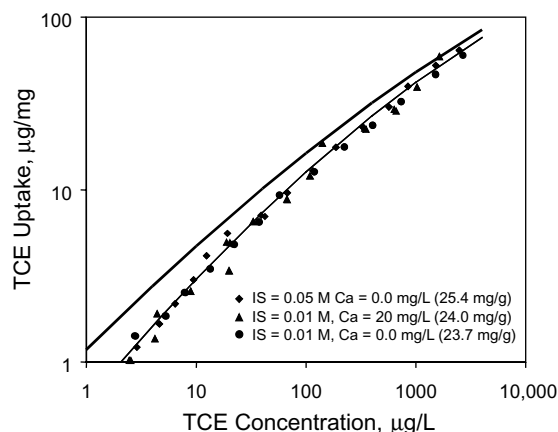


Fig. 6. TCE uptake by carbon preloaded at different ionic strengths, different initial humic acid solution concentrations, and different calcium ion concentrations, but yielding similar humic acid loadings. Lines represent the Dubinin–Astakhov isotherm fitted to pooled data. The isotherms measured in this study are compared to those measured at ionic strength (IS) = 0.01 M, Ca = 0.0 M, reported by Kilduff et al. [8].

the same. (It should be noted, however, that humic acid loading is significantly greater when calcium is present—other factors such as initial humic acid concentration and solution ionic strength being equal). These results were somewhat unexpected, given that calcium can interact specifically with humic substance functional groups (e.g., complex formation) while sodium does not.

As discussed by Kilduff et al. [33], it is likely that calcium can complex humic substances in solution, prior to the adsorption step. Evidence was also provided for aggregation of humic molecules, possibly through bridging of humic molecules by calcium ions. These mechanisms would tend to *increase* the size distribution of humic acid components, reducing their ability to access micropores. The fact that calcium increases the extent of humic acid adsorption in opposition to aggregation effects suggests that larger molecules are being adsorbed, smaller molecules are being adsorbed more effectively, or both. Both explanations are likely because the divalent cation has a greater ability to screen charge, and because new adsorption sites may be created on the surface via cation bridges. While the net effect is to increase the loading of humic acid, it does not appear that the mechanism of competition between adsorbed humic substances and TCE is changed significantly. It should also be noted that significant effects of calcium can occur even when the calcium concentration is relatively low. This conclusion is supported by the statistically similar Freundlich isotherm parameters for TCE uptake by carbon preloaded in the presence of calcium concentrations ranging from 0.05 to 1.0 mM (2 to 40 mg/L).



Table 2  
Effect of calcium content on HA preloading

Preloading conditions			Dubinin isotherm parameters and statistics			Freundlich isotherm parameters and statistics		
Ca, mg/L <sup>a</sup>	C <sub>0</sub> , mg TOC/L	q <sub>e</sub> , mg TOC/g	Param.	Param. Est. <sup>b</sup>	95% CI <sup>c</sup>	Param.	Param. Est. <sup>b</sup>	95% CI <sup>c</sup>
2	19.3	11.1	$Q^0$	351	215–487	$K_F$	0.772	0.707–0.842
			$n$	1.64	1.47–1.82	$n$	0.631	0.598–0.665
			$B$	53.7	17.1–90.3			
10	19.0	13.0	$Q^0$	384	237–530	$K_F$	0.818	0.773–0.867
			$n$	1.58	1.42–1.75	$n$	0.628	0.606–0.650
			$B$	43.6	15.7–71.5			
20	19.1	13.1	$Q^0$	278	152–404	$K_F$	0.804	0.743–0.870
			$n$	1.79	1.55–2.04	$n$	0.667	0.631–0.702
			$B$	96.0	6.5–185			
20	10.0	8.2	$Q^0$	500	184–816	$K_F$	1.02	0.947–1.11
			$n$	1.45	1.22–1.68	$n$	0.587	0.556–0.619
			$B$	27.0	2.34–51.7			
20	38.8	24.0	$Q^0$	328	108–547	$K_F$	0.613	0.542–0.693
			$n$	1.68	1.36–1.99	$n$	0.690	0.644–0.737
			$B$	60.0	0.0–132.2			
40	18.9	14.4	$Q^0$	488	205–771	$K_F$	0.717	0.672–0.765
			$n$	1.48	1.26–1.70	$n$	0.630	0.607–0.653
			$B$	28.8	4.34–53.3			
80	18.9	17.1	$Q^0$	500	80.7–919	$K_F$	1.15	1.04–1.27
			$n$	1.43	1.13–1.74	$n$	0.585	0.543–0.627
			$B$	26.3	0.0–57.9			

<sup>a</sup>Ca: Total calcium ion concentration (free + bound) in the preloading reactor.

<sup>b</sup>Isotherm parameters correspond to uptake in units of µg/mg and concentration in units of µg/L.

<sup>c</sup>CI: Confidence interval.

Conditions: Ionic strength was 0.01 M, adjusted with NaCl, in all preloading and isotherm reactors.

Adsorbent dose was 1.05 g/L for all preloading reactors.

The carbon preloaded in the presence of 2 mM calcium did not exhibit any statistically significant reduction in TCE adsorption capacity. A brown precipitate was observed in this reactor and the TOC concentration after equilibration was only 0.8 mg/L. Therefore, removal of TOC from solution was apparently caused by both adsorption and precipitation. The high calcium concentration may have destabilized the larger molecular-weight humic components causing aggregation and subsequent removal from solution. It is also possible that a calcium precipitate formed, and humic molecules may have associated with the precipitate by an adsorption or enmeshment mechanism. Therefore, it is likely that a significant fraction of the reactive molecular sizes were removed from solution but were not adsorbed by the carbon. Based on the evidence for aggregation observed in the molecular-weight distributions reported by Kilduff et al. [33], another likely explanation is that otherwise reactive molecules were aggregated to form larger species which could not access micro- and meso-pores within the carbon structure.

In the experiments described thus far, increases in calcium concentration were associated with increases in

the amount of humic acid adsorbed. An experiment was designed to investigate the effect of calcium for a constant adsorbed amount of humic material. Carbon was preloaded in the absence of calcium to a loading of 16.9 mg TOC/g and recovered from the preloading reactor. This preloaded carbon was then used in a TCE adsorption experiment with a background solution that did contain calcium. In this experiment, the presence of calcium could have no effect on the amount of humic acid adsorbed. The isotherms developed in this experiment are shown in Fig. 7; experimental conditions and isotherm parameters are shown in Table 3. The presence of calcium in the buffer during TCE adsorption resulted in a statistically significant decrease in the Freundlich  $K_F$  and an increase in  $n$ . This result suggests that the presence of calcium can increase the ability of preloaded humic material to compete with TCE. The changes in the Freundlich parameters suggest that the effect of calcium on the impact of preloading is to further deplete high-energy sites, which remain available in the absence of calcium. Apparently, the association of calcium with humic acid can occur after the humic material has been adsorbed. It is not possible to determine from the data if the sorption of calcium is

kinetically favored, or whether sorption of calcium and TCE occur simultaneously. In either case, it is likely that the presence of calcium promotes configurational changes in the adsorbed DOM, or cation bridging with the formation of new binding sites for the humic acid, which either block TCE access or displace adsorbed TCE. These mechanisms appear fundamentally different than those that occur in the absence of calcium. However, the significance of this difference seems to depend on the order in which calcium is input to the system. As discussed previously, when calcium associates with humic acid in solution prior to humic acid adsorption, the subsequent impact of preloading on TCE uptake is primarily correlated with humic acid loading.

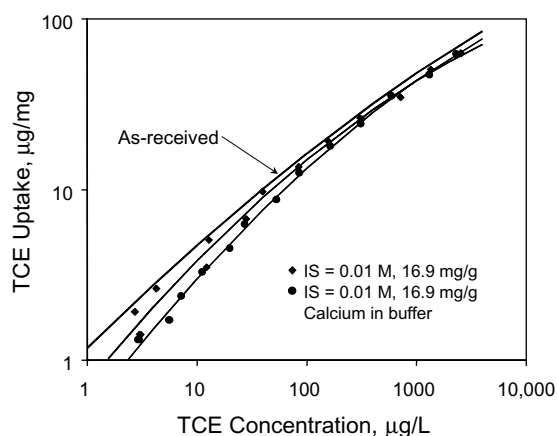


Fig. 7. The effect of calcium for a constant adsorbed amount of humic material, 16.9 mg TOC/g. Lines are fits to the data using the Dubinin–Astakhov isotherm. Carbon was preloaded in the absence of calcium, which was added during TCE sorption.

### 3.4. Effects of dissolved oxygen concentration during preloading

The presence of dissolved oxygen has been shown to increase the uptake of natural organic matter, natural humic and fulvic acids, and other model compounds (e.g., PMA) from aqueous solution [26,42,43,45,46]. While the mechanism for the observed increases in uptake is difficult to identify conclusively, one possible explanation is that such compounds undergo oxidative coupling reactions that are catalyzed by carbon surfaces, by analogy to the effects of dissolved oxygen on the uptake of phenolic compounds [42,46–48]. Control experiments have confirmed that measurable oxidative coupling does not occur in solution for the experimental conditions and equilibration times studied here (data not shown). If oxidative coupling occurs among smaller molecular-size components, reducing the ability of humic acid to diffuse into micropores, the impacts of preloading could conceivably be reduced in the presence of oxygen (even if humic acid loading is increased). However, it is also possible that such coupling could serve to block access by TCE to adsorbent sites (micropores), or could compete directly for high-energy sites if covalent bonds formed directly between adsorbed natural organic matter and the adsorbent surface. Control experiments confirmed that there was no effect of dissolved oxygen alone (in the absence of humic acid) on TCE uptake, i.e., TCE is not oxygen sensitive (data not shown).

The experimental conditions for oxic and anoxic preloading, and isotherm model parameters are shown in Table 4. The mass of PMA loaded is somewhat lower than the Laurentian humic acid; however, there is a clear trend of decreasing Freundlich  $K_F$  and increasing  $n$  with an increase in the PMA loading. The decrease in  $K_F$  is statistically significant for all cases except the carbon

Table 3  
Effect of calcium order of addition on HA preloading

Preloading conditions			Dubinin isotherm parameters and statistics			Freundlich isotherm parameters and statistics		
Ca, mg/L <sup>a</sup>	C <sub>0</sub> , mg TOC/L	q <sub>e</sub> , mg TOC/g	Param.	Param. Est. <sup>b</sup>	95% CI <sup>c</sup>	Param.	Param. Est. <sup>b</sup>	95% CI <sup>c</sup>
0.0	55.4	16.9	$Q^0$	171	86–57	$K_F$	0.941	0.815–1.09
			$n$	2.01	1.64–2.38	$n$	0.606	0.551–0.661
			$B$	225	0.0–5342			
20.0	55.4	16.9	$Q^0$	219	161–277	$K_F$	0.556	0.515–0.600
			$n$	1.93	1.77–2.10	$n$	0.711	0.682–0.740
			$B$	155	59.0–251			

<sup>a</sup>Ca: Initial calcium ion concentration in solution during TCE adsorption only. Calcium ion concentration in the preloading reactor was zero.

<sup>b</sup>Isotherm parameters correspond to uptake in units of µg/mg and concentration in units of µg/L.

<sup>c</sup>CI: Confidence interval.

Conditions: Ionic strength was 0.01 M, adjusted with NaCl, in all preloading and isotherm reactors.

Adsorbent dose was 1.05 g/L for during preloading.

Table 4  
Effect of dissolved oxygen on PMA preloading

Preloading conditions		Dubinin isotherm parameters and statistics			Freundlich isotherm parameters and statistics		
O <sub>2</sub> State <sup>a</sup>	q <sub>e</sub> , gTOC/kg	Param.	Param. Est. <sup>b</sup>	95% CI <sup>c</sup>	Param.	Param. Est. <sup>b</sup>	95% CI <sup>c</sup>
OXIC	0.0	Q <sup>0</sup>	353	220–485	K <sub>F</sub>	1.58	1.48–1.70
		n	1.55	1.37–1.74	n	0.549	0.523–0.575
		B	44.4	12.7–76.1			
OXIC	7.3	Q <sup>0</sup>	398	239–557	K <sub>F</sub>	1.01	0.93–1.10
		n	1.43	1.27–1.59	n	0.574	0.542–0.605
		B	26.3	9.8–42.9			
OXIC	11.3	Q <sup>0</sup>	270	145–396	K <sub>F</sub>	1.12	1.00–1.26
		n	1.61	1.37–1.86	n	0.571	0.525–0.618
		B	54.9	4.05–106			
OXIC	13.9	Q <sup>0</sup>	257	150–364	K <sub>F</sub>	0.913	0.81–1.03
		n	1.65	1.43–1.88	n	0.600	0.556–0.644
		B	61.3	9.19–113			
ANOXIC	5.2	Q <sup>0</sup>	385	197–572	K <sub>F</sub>	1.33	1.20–1.49
		n	1.48	1.26–1.71	n	0.545	0.512–0.579
		B	33.0	4.31–61.7			
ANOXIC	8.4	Q <sup>0</sup>	220	130–310	K <sub>F</sub>	1.27	1.16–1.39
		n	1.75	1.50–2.00	n	0.566	0.534–0.598
		B	94.2	4.53–184			
ANOXIC	8.6	Q <sup>0</sup>	152	77.8–227	K <sub>F</sub>	1.13	0.93–1.38
		n	2.17	1.72–2.61	n	0.621	0.546–0.696
		B	425	0.0–1121			

<sup>a</sup> Oxygen state: Oxic means dissolved oxygen concentrations near saturation, 8 mg/L; Anoxic means oxygen free.

<sup>b</sup> Isotherm parameters correspond to uptake in units of µg/mg and concentration in units of µg/L.

<sup>c</sup> CI: Confidence interval.

Conditions: Ionic strength was 0.01, adjusted with NaCl, and calcium content was zero in all preloading reactors.

Adsorbent dose was 1.05 g/L for all preloading reactors.

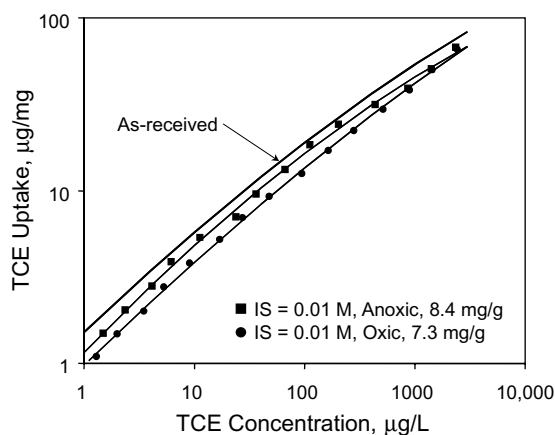


Fig. 8. The effect of oxygen concentration for similar adsorbed amounts of oxygen-sensitive PMA. Lines are fits to the data using the Dubinin–Astakhov isotherm.

preloaded under anoxic conditions with 5.2 mg PMA/g. The Freundlich *n* increases by up to 13%, but the increase is not statistically significant. Fig. 8 shows isotherms measured using carbon preloaded under

different dissolved oxygen concentrations, but yielding similar PMA loading. In contrast to the effects of ionic composition, these data suggest that the presence of dissolved oxygen *does* fundamentally change the mechanism by which humic acid competes with TCE; TCE uptake is lower when preloading occurs in the presence of dissolved oxygen, even when the amount of PMA loaded is the same. One explanation invokes an oxidative coupling mechanism promoted by the carbon surface, which results in either additional blockage of TCE sorption sites, additional site competition, or both. While the data are consistent with this mechanism, providing proof is difficult. Surface spectroscopic techniques could provide useful information, but micropore surfaces are difficult to probe. Size exclusion chromatography of desorbed NOM could provide evidence of changes in molecular weight, but NOM and similar model compounds such as PMA do not readily desorb, precluding such analyses.

The effects of dissolved oxygen on the impact of preloading found in this research may be lower on other carbons that contain an appreciable density of oxygen containing functional groups on their surface. The F400 carbon used in this research has a low surface acidity, a

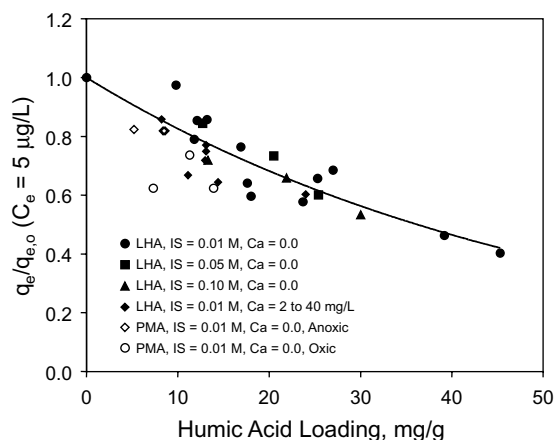


Fig. 9. The effect of preloading is evaluated in terms of TCE uptake by preloaded carbon, as a fraction of the as-received uptake,  $q_e/q_{e,0}$ , both evaluated at the US drinking water standard of  $C_e = 5 \text{ mg/m}^3$ . Data for LHA, ionic strength (IS) = 0.01 M, Ca = 0.0 M, were reported previously by Kilduff et al. [8].

characteristic that has been correlated with poor regenerability of phenolic compounds, possibly resulting from oxidative coupling reactions [56]. More oxidized carbons exhibited more complete phenol sorption reversibility, suggesting that the extent of oxidative coupling reactions was significantly reduced (although not completely eliminated). Although not investigated in this work, it is possible that the effects of oxygen on the impact of preloading would be less if the carbon surface acidity were greater. This is currently being investigated in our laboratories.

The reduction in TCE uptake by preloaded carbon as a fraction of the as-received uptake at the same  $C_e$ , was plotted for all the preloading conditions evaluated in this study. These data are plotted versus the uptake of humic acid or PMA in Fig. 9. Despite some scatter in the data, the impact of preloading on TCE uptake under most of the conditions studied is well described by the empirical correlation shown in Fig. 4. The impact of preloaded PMA (under anoxic conditions) is remarkably similar to the impact of preloaded humic acid, even though PMA is widely regarded as a surrogate for fulvic acid. The preloading conditions that exhibit the greatest deviation from the general trend depicted in Fig. 9 include the PMA under oxidic conditions. Based on this observation, and the data for the effect of calcium shown in Fig. 7, it appears that solution components (dissolved oxygen, calcium added after NOM adsorption) that have the ability to modify the structure of natural organic matter after it has been adsorbed can significantly change the mechanism by which NOM competes with TCE. In contrast, solution components that modify the configuration of natural organic matter in solution

(ionic strength, calcium present during NOM adsorption), potentially increase the uptake of NOM, but do not change the mechanism by which it competes with TCE. In such cases, reductions in TCE uptake correlate with natural organic matter loading.

#### 4. Conclusions

TCE adsorption isotherms were measured on F400 carbon preloaded with Laurentian humic acid and synthetic PMA under a wide variety of conditions. The uptake of organic matter increased with increasing solution ionic strength, calcium concentration (until solubility was exceeded) and dissolved oxygen. As a consequence, greater reductions in TCE adsorption occurred for a given percentage of TOC removal. In terms of ionic composition, the reduction in TCE adsorption was fundamentally related to the amount of humic material adsorbed, independent of the ionic strength or calcium concentration during preloading. When the amount of adsorbed humic acid was similar, the Freundlich  $K_F$  and  $n$  values were statistically similar for all ionic compositions. However, calcium ions exhibited two features that were distinct from this general trend.

First, the effects of calcium depended on the order of addition; when calcium was absent during preloading, but present during subsequent TCE adsorption, the effects of preloading were greater, even though the humic acid loading was the same. This suggests that the calcium ion can associate with humic material after the humic has been adsorbed, possibly promoting stronger binding between humic acid and the carbon surface, or facilitating humic substance conformational changes, which subsequently reduces TCE uptake. The formation of new adsorption sites would represent a mechanism fundamentally different than that which occurs in the absence of calcium. Second, when calcium was present in concentrations sufficient to induce precipitation, the subsequent aggregation or co-precipitation of humic acid mitigated the effects of preloading; uptake of TCE by carbon preloaded under these conditions was similar to as-received carbon.

In contrast to the effects of ionic composition, these data suggest that the presence of dissolved oxygen *does* fundamentally change the mechanism by which organic macromolecules compete with TCE; TCE uptake is lower when preloading occurs in the presence of dissolved oxygen, even when the amount of PMA loaded is the same. One explanation invokes a coupling mechanism promoted by the carbon surface, which results in either additional blockage of TCE sorption sites, additional site competition, or both.

We believe that the findings of this research using a batch reactor system should be generally applicable to

other reactor configurations. However, further investigation is warranted to assess how the effects of solution composition on the reductions in TCE uptake due to preloading manifest in fixed-bed reactors. For example, the nature and impacts of such phenomena as chromatographic separation of NOM components will be different in fixed bed systems, and various NOM components may exhibit distinct responses to solution composition. Future work in this area will assess the extent to which the findings of this research can be employed to predict the competitive effects of preloading in full-scale column systems.

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